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Photophysical properties of flavones in different environments

Munna Sarkar and Pradeep K Sengupta*
Nuclear Chemistry Division, Saha Institute of Nuclear Physics,
1/AF, Bidhannagar, Calcutta-700 064, India

Abstract : Flavones and related compounds are of widespread occurrence in higher plants, where they perform several functions. In addition, many flavone derivatives have attracted considerable interest for their novel features as antitumour agents, and other useful pharmacological applications. In order to use electronic spectroscopy to probe the nature of these compounds with cellular receptor sites, we have undertaken an investigation of the photophysical properties of some model flavones. In the present paper we report some preliminary results of their luminescence behaviour in different solvents and in micellar systems. The emission characteristics of one such model compound 7-hydroxyflavone (7HF) shows a strong dependence on hydrogen bonding effects, viscosity and polarity of the media. The dual emission properties of 7-hydroxyflavone (7HF) and 3-hydroxyflavone (3HF) have been used to probe the environment in micelles.

Keywords : Fluorescence, photophysics, flavones, different environments.

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1. Introduction

Flavones and related compounds form a large group of biologically active organic natural products, which are widely distributed in plants of higher genera. In addition to their primary role as pigments of flowers and fruits these compounds are involved in many other biologically important activities. For example, some of these compounds are known to have protective effects on photosensitized lysis of human erythrocytes (Sorata *et al* 1988), and also prevent blood cell adhesion and aggregation. More recently, some of the flavone derivatives viz. flavone acetic acids, have been reported to be highly active against a variety of transplantable solid tumours (Thomson and Higgins 1988, Kato *et al* 1983). Their antitumour activities are found to be strongly dependent on the position and nature of the substituents, which suggest that conformational and/or electronic effects might be very important in determining their antitumour activities. In order to use electronic spectroscopy (luminescence and/or absorption) to explore the interaction of flavones with cellular receptor sites, it is necessary to have a detailed understanding of the photophysical

*Present address : Biophysics Division, Saha Institute of Nuclear Physics, 37, Belgachia Road, Calcutta-700 037, India.

properties of flavones in different environments. Various aspects of the excited state relaxation processes in different hydroxyflavones especially excited state proton transfer (ESPT) (Sengupta and Kasha 1979, Sengupta 1980, Schipfer *et al* 1981, Wolfbeis *et al* 1984, Itoh and Adachi 1984) and solvent dipolar relaxation effects (Sarkar and Sengupta 1989, 1990), have received considerable attention in recent years.

In the present work 7-hydroxyflavone (7HF) has been chosen as a prototype model compound for investigations on the photophysical properties of naturally occurring flavones. We have examined the electronic absorption and luminescence spectra of 7HF in different solvent media (protic as well as aprotic) and in SDS micelles, the latter serving as a representative for membrane mimetic environment. Besides 7HF, we also present some results on the related compound 3-hydroxyflavone (3HF) in SDS micelles.

2. Experimental

7HF and 3HF were purchased from Aldrich Chemical Company. The solvents ethyl acetate (Merck), acetonitrile (Aldrich), methanol (E. Merck), 1-propanol (Aldrich), 2,2,2,-trifluoroethanol (Aldrich) and glycerol (Merck) were of the highest grades available. Sodium dodecyl sulphate (SDS) was obtained from Sigma Chemical Company. The concentrations of 7HF and 3HF were 2×10^{-5} M in all solutions.

Electronic absorption and emission spectra were recorded with a Perkin-Elmer Model 554 spectrophotometer and Hitachi Model F-4010 spectrofluorometer respectively. The relative quantum yields were measured using quinine sulphate in 0.1N H_2SO_4 ($\varphi_F = 0.546$). All measurements were carried out at room temperature.

3. Results and discussion

Figure 1 shows the absorption spectra of 7HF in various protic as well as aprotic solvents. The corresponding fluorescence emissiom spectra are given in Figure 2. Both absorption and emission characteristics of 7HF show a strong dependence on the nature of the solvent. In protic solvents like methanol and 1-propanol 7HF exhibits its characteristic dual emission as reported earlier (Schipfer *et al* 1981, Wolfbeis *et al* 1984, Itoh and Adachi 1984, Sengupta 1980), with a green emission with $\lambda_{max} \sim 530$-540 nm and a blue-violet emission with $\lambda_{max} \sim 390$-420 nm. In aprotic polar solvents like ethyl acetate and acetonitrile emission is extremely weak. Intense blue fluorescence ($\lambda_{max} \sim 409$ nm) is observed in strongly hydrogen-bonding solvents like 2,2,2-trifluoroethanol (TFE). Interestingly the green emission is not observed in this case. Table 1 lists the relative quantum yields of 7HF in these solvents. A large variation is observed in the relative quantum yield values from ~ 0.0001 in ethyl acetate to 0.08 in TFE.

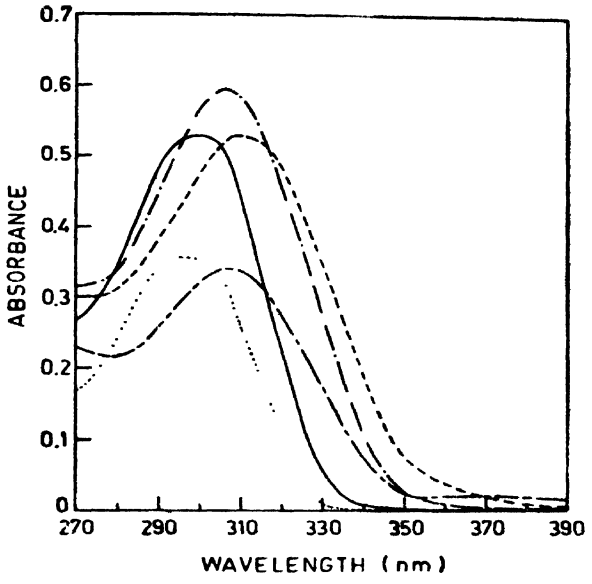

Figure 1. Absorption spectra of 7HF in different solvents: ethylacetate (···); acetonitrile (——), methanol (– —), 1-propanol (— - —), 2,2,2-trifluoroethanol (- - - -).

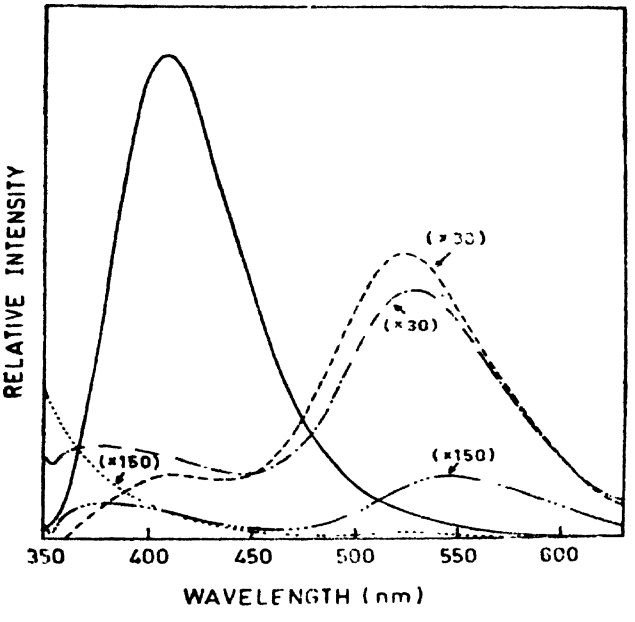

Figure 2. Emission spectra of 7HF in different solvents (λ_{exc}=320 nm): ethylacetate (···), acetonitrile (— ··· —), methanol (— —), 1-propanol (- - -), 2,2,2-trifluoroethanol (——).

The dual emission behaviour of 7HF has been extensively studied by earlier workers (Schipfer *et al* 1981, Wolfbeis *et al* 1984, Itoh and Adachi 1984). The blue-violet emission is attributed to the $S_1(\pi\pi^*) \rightarrow S_0$ transition from the

Table 1. Relative quantum yields (ϕ_f) of 7HF in different solvents.

Solvents	ϕ_f(a)
1. Ethyl acetate	~0.0001
2. Acetonitrile	~0.0002
3. Methanol	0.0019
4. 1-Propanol	0.0032
5. 2,2,2-Trifluoroethanol	0.0800

(a) Quinine sulphate in 0.10 N H_2SO_4 was taken as standard ($\phi_f = 0.546$).

neutral solvated 7HF molecule (Schipfer *et al* 1981, Wolfbeis *et al* 1984); whereas the green emission is due to the excited state proton transfer (ESPT) tautomer. According to Itoh *et al* (Itoh and Adachi 1984) the green band is due to emission from ESPT species which involves a proton abstraction from the hydroxy group with the subsequent protonation of either the carbonyl or the heterocyclic oxygen in the benzopyrone ring. The low fluorescence quantum yield of 7HF in aprotic polar solvents like ethyl acetate and acetonitrile may be due to efficient internal conversion between S_1 and S_0 states. This may result from vibronic interaction between singlet ($\pi\pi^*$) and ($n\pi^*$) levels lying in close proximity (Wassam and Lim 1977, 1978, Lai *et al* 1982). Further investigations are being carried out in order to explore this aspect in greater detail. In TFE which is a strongly hydrogen bonding solvent, the absence of dual emission can be explained as follows. It has been shown by Itoh *et al* (Itoh and Adachi 1984) that the precursor to the ESPT process, responsible for the green emission is 1 : 2 complex of 7HF with methanol, probably through hydrogen-bonding interaction. In TFE the H-bond between the hydroxylic proton of the solvent and the heterocyclic or carbonyl oxygen of 7HF will be stronger, whereas the H-bond between the proton of the hydroxy group of 7HF and the O-atom in the hydroxy group of the solvent will be weaker. This may prevent deprotonation of 7HF in the excited state resulting in the absence of green emission band.

Figure 3 shows the increase in intensity of the higher energy emission band (I_N) with increasing viscosity in glycerol-water mixtures. The role of increased viscosity in enhancing fluorescence efficiency is due to the viscosity dependent nonradiative internal conversion $S_1 \rightarrow S_0$ that decreases in viscous medium, which minimize the twisting molecular motion of the phenyl ring in the excited state (Song *et al* 1972, El-Bayoumi 1976).

Figure 4 shows the dependence of blue-violet emission of 7HF (I_N) on increasing surfactant (SDS) concentration. The curve shows a break around the critical micelle concentration (CMC) value of SDS. Linear extrapolation gave

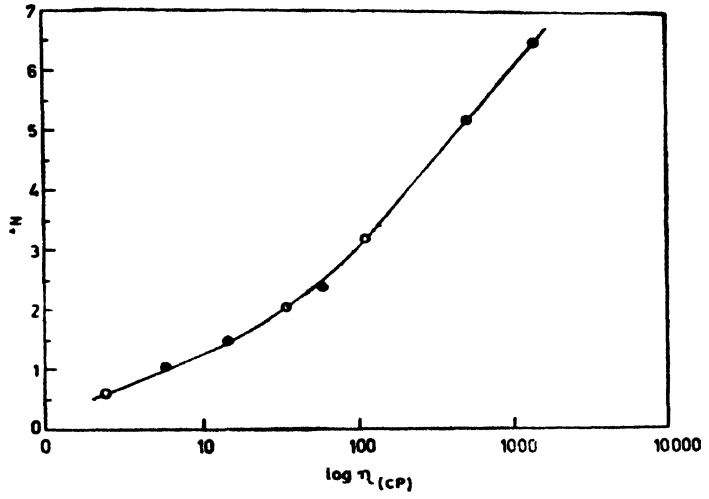

Figure 3. Viscosity dependence of emission intensity of 7HF (λ_{exc} = 310 nm).

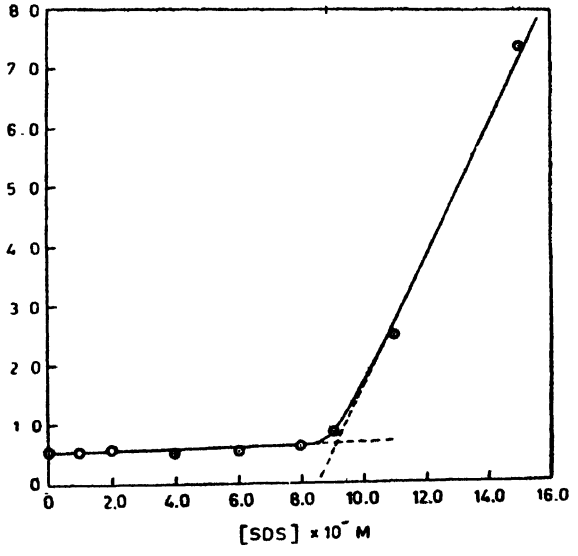

Figure 4. Dependence of emission intensity of 7HF on SDS concentration (λ_{exc} = 310 nm).

a CMC value of SDS ~ 9.0×10^{-3} M which is in reasonably good agreement with the literature values (Fendlar 1982). In case of 3HF excited state intramolecular proton transfer (ESIPT) tautomer emission (Sengupta and Kasha

1979, McMorrow and Kasha 1984, Kasha 1986) with maximum at ~ 520 nm shows a large enhancement in the intensity with increasing surfactant concentration. The abrupt change in the intensity of the ESIPT tautomer which we observed around the CMC value of SDS enables us to use 3HF as a probe of the micellar environment.

Further work is in progress to get a better insight regarding the photophysics of these molecules in different biomimetic environments and in low temperature rigid glasses.

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